Topological analysis of zeolite-like compounds with mixed frameworks and crystal structure prediction using the approach of OD (“order-disorder”) theory

Sergey M. Aksenov1* and Stefano Merlino2

1Kola Science Centre RAS, Apatity, Russia
2Accademia Nazionale dei Lincei, Rome, Italy

*aks.crys@gmail.com

Compounds with the general formula Cs\(^{[6]}\)Al\(^{[4]}\)\(\{\text{TP}_6\text{O}_{20}\}\) (where \(T = \text{B}, \text{Al}\) [2]) are considered as polytypes. The crystal structures of compounds with the general formula Cs\(^{[6]}\)Al\(^{[4]}\)\(\{\text{TP}_6\text{O}_{20}\}\) were determined by means of natural tilings (the smallest polyhedral cationic clusters that form a framework) of the 3D cation nets [9] calculated using the ToposPro software [10].

The symmetrical relations between the compounds have been analyzed using the OD theoretical approach [3,5,6] for the OD families containing more than one \((M > 1)\) kinds of layers [7]. The OD layers have been chosen in accordance with the equivalent region (ER) requirements [8]. Topological analysis of the frameworks was performed by means of natural tilings (the smallest polyhedral cationic clusters that form a framework) of the 3D cation nets [9] calculated using the ToposPro software [10].

The crystal structures of compounds with the general formula Cs\(^{[6]}\)Al\(^{[4]}\)\(\{\text{TP}_6\text{O}_{20}\}\) (where \(T = \text{Al, B}\)) display order-disorder (OD) character and can be described using the same OD groupoid family [11]. Their structures built up by two kinds of non-polar layers, with the layer symmetries \(Pc(n)2\) (\(L_{2n+1}\)-type) and \(Pc(a)m\) (\(L_{2n}\)-type) (category IV [7]). Layers of both types \((L_{2n} \text{ and } L_{2n+1})\) alternate along the \(b\) direction and have common translation vectors \(a\) and \(c\) \((a \sim 10.0\ \text{Å}, \ c \sim 12.0\ \text{Å})\). All ordered polytypes as well as disordered structures can be obtained using the following partial symmetry operators that may be active in the \(L_{2n}\) type layer: the \(2_1\) screw axis parallel to \(c\) \([\sim \sim 2_1]\) or inversion centers and the \(2_1\) screw axis parallel to \(a\) \([2_1 \sim \sim]\). The symmetry relation common to all polytypes of this family are described by the OD groupoid family symbol:

\[
Pc(n)2 \quad \begin{array}{cc}
2_1/c (2/a) & 2_1/m \\
r, 0
\end{array}
\]

(1)

where \(r = 0\); the first line contains the layer-group symbols of the two constituting layers, while the second line indicates positional relations between the adjacent layers [12].

Different sequences of operators active in the \(L_{2n}\) type layer \((\sim \sim - \sim 2_1)\) screw axes or inversion centers and \([2_1 \sim \sim \sim]\) screw axes) define the formation of multilayered structures with the increased \(b\) parameter, which are considered as non-MDO polytypes.

Compounds with the general formula Rb\(^{[6]}\)\(M^{2+}\)[\(^{[4]}\)\(\text{TP}_6\text{O}_{20}\)] \((M = \text{Al, Ga}; \ T = \text{Al, B})\) are based on heteropolyhedral \(MT\)-frameworks with the same stoichiometry as in Cs\(^{[6]}\)Al\(^{[4]}\)\(\{\text{TP}_6\text{O}_{20}\}\) (where \(T = \text{Al, B}\)). It was found that all the frameworks have common natural tilings, which indicates the close relationships of the two families of compounds.

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References:


